Aqueous or Slow Release? - Considerations for Substrate Selection

Kent S. Sorenson, Jr.
North Wind, Inc.
P.O. Box 51174, Idaho Falls, ID 83405
(208) 557-7829, email: ksorenson@nwindenv.com

Introduction

A primary focus of the research on bioremediation of chlorinated solvents for the last several years has been the evaluation and development of a variety of electron donors. While many of these have one or more desirable qualities, no electron donor has been demonstrated to be suitable for all sites. With the huge variety of electron donors to choose from, the selection of one for a particular site can be a daunting task. The result is that decisions are often based on familiarity, popularity, or convenience without sufficient consideration of site-specific remediation goals, hydrogeologic conditions, and contaminant fate and transport. The goal of this presentation is to provide some guidance that will help simplify the selection process so that site managers and remediation professionals can make more informed, technically sound decisions about electron donors.

Selection Factors

Many factors should be considered in choosing an appropriate electron donor for a given site. Broadly, these factors relate to both site-specific conditions and the properties of the electron donors being considered. The goal, of course, is to select the donor whose properties best suit the site conditions. Several important factors are: application type, distribution requirements, presence or absence of residual nonaqueous contaminants, vertical extent of contamination, aquifer buffering capacity, land use, donor impact on dechlorination efficiency, donor purity, and cost. Although cost is ultimately the most important selection factor, it is placed last in this list because it can only be appropriately evaluated when all of the other factors are considered.
Now it appears that site managers are faced not only with a long list of possible electron donors, but with an equally long list of selection factors to be considered. The process can be simplified, however, because the universe of electron donors can generally be divided into two classes that are referred to herein as aqueous and slow-release. The properties of these classes of electron donors, and how they match up with various site-specific conditions are discussed below.

Aqueous Electron Donors

The first class of electron donors considered is aqueous electron donors, or those that are highly soluble in water. These include compounds such as lactate, propionate, butyrate, acetate, benzoate, molasses, whey, or various alcohols. Many of these are available in multiple forms such as salts or acids. Four general properties of electron donors are summarized in Table 1. Aqueous electron donors, by definition, have a high solubility in water. As would be expected for such compounds, they generally have a low viscosity (near that of water) except at very high concentrations. The density of aqueous electron donors can range from slightly less than that of water to that of dense nonaqueous phase liquids (DNAPLs) such as TCE for high concentration salts. Finally, aqueous electron donors vary in their impact on bioavailability. While recent research has shown that reductive dechlorination facilitated by any electron donor accelerates dissolution of NAPLs due to its effect on concentration gradients and the solubility of less chlorinated degradation products (Carr et al. 2000, Yang and McCarty 2000, Cope and Hughes 2001), some aqueous electron donors have the potential to increase effective solubility of the parent compounds by decreasing the interfacial tension between the aqueous and nonaqueous phases (Sorenson 2002).

Table 1. General properties of electron donors.

Property	Aqueous Electron Donors	Slow-Release Electron Donors
Solubility in Water	High	Low
Viscosity (water is considered low)	Low	High (or solid)
Density (water is considered low)	Low to High	Low to High
Impact on Bioavailability	Low to High	Low[1]

[1]While this is generally true, new slow-release donors are in development that may have a high impact on bioavailability

The general properties of aqueous electron donors have several important implications for their use. First of all, their high solubility and low viscosity makes them relatively easy to distribute by advection in the subsurface. An example of this is shown in Figure 1. Sodium lactate was distributed throughout an area of TCE contamination approximately 1800 ft long and 900 ft wide using only nine injection wells manifolded to a single injection pump. The electron donor distribution shown is based on chemical oxygen demand concentrations almost two months after a lactate injection. Concentrations were greater than 1000 mg/L over most of the area, which rapidly facilitated the onset of the strongly reducing conditions required for dechlorination. The rapid shift in redox conditions that can be achieved with relatively high electron donor concentrations over large areas is another potential benefit because the extent of dechlorination is often limited by inadequate redox conditions.

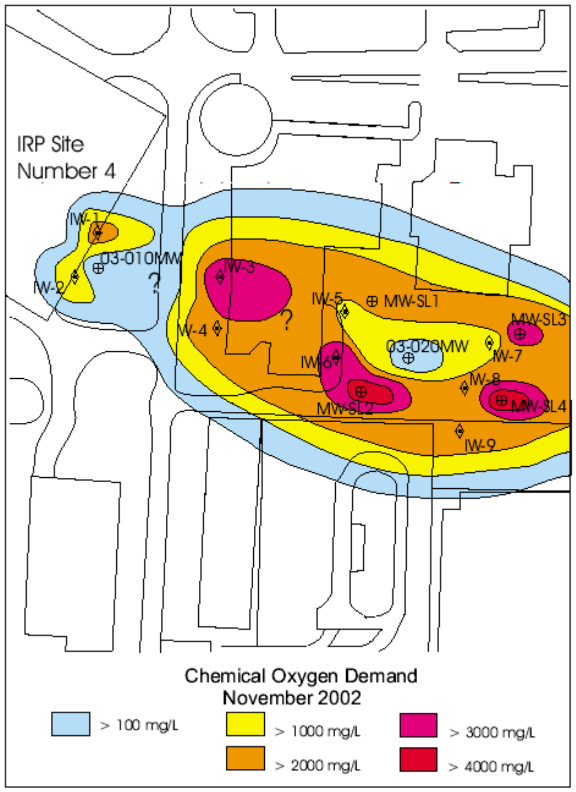

FIGURE 1. Large-scale lactate distribution with few injection wells (*courtesy SAIC*).

The variable density of aqueous electron donors can also be used for the benefit of certain applications. While many of these donors have near-neutral buoyancies, some are heavier than water, as mentioned in Table 1. This property can be used to treat aquifers having large thicknesses with partially penetrating wells. In some cases it may be useful that higher density donors will tend to migrate in a similar fashion to DNAPLs. Another potential application of higher density donors is infiltration. Where the water table is shallow, it may be very cost-effective to distribute an electron donor solution by infiltration. This may be particularly applicable when the original source of contamination was a pit, sump, or pond.

While the high solubility of aqueous electron donors has several benefits, it does mean that their longevity is somewhat limited. Sodium lactate, for example typically lasts from 1 to a few months depending on the concentration injected and ground water velocity. In the example of Figure 1, the injection frequency was initially every two months, which was found to be more often than necessary for longer-term operations. While this longevity is less than slow-release electron donors, it is still significant. Aqueous electron donors such as propionate and butyrate would be expected to have somewhat longer longevities because their fermentation to hydrogen is thermodynamically limited (Fennell et al. 1997). Thus, subsurface longevities of aqueous electron donors vary, but are generally on the order of months.

The enhanced bioavailability provided by some aqueous electron donors is a very important property. As mentioned above, some aqueous electron donors reduce the interfacial tension between nonaqueous chlorinated solvents and the aqueous phase. This effect is generally a function of the concentration of the electron donor solution. The injection of aqueous donors with this property for the purpose of accelerating the partitioning of solvents into the aqueous phase is known as Bioavailability Enhancement Technology™, or B.E.T.™ (patent pending). This is useful in residual source areas where immobile NAPL is trapped in small pore spaces, or where large quantities of sorbed contamination are present. Thus, bioremediation can be used for accelerated mass removal in source areas that do not have large volumes of free product, while still retaining the benefits of a relatively passive, in situ technology. Another potential application is for "polishing" the residual DNAPL in a source area where a more aggressive technology has been used to remove free product.

Slow-Release Electron Donors

The second class of electron donors considered is slow-release electron donors. These include compounds such as HRC®, vegetable oil, polymeric organics such as chitin or bark mulch, and LactOil™. As noted above, some of the general properties of these donors are summarized in Table 1. Slow-release electron donors either have a low solubility in water, or at least dissolve very slowly. They generally have a high viscosity, or are solids. Liquid slow-release electron donors generally have densities slightly less than water in the case of some oils, to about the same as water. Most slow-release electron donors have a limited impact on bioavailability. When dechlorination is effectively stimulated, they facilitate some accelerated dissolution due to increased concentration gradients and the solubility of less chlorinated degradation products, as mentioned above. Most do not actually increase effective solubility through the decreased interfacial tension mechanism, however.

The low solubility of these donors ensures relatively long lifespans in the subsurface, which has been their primary attraction. For example, it is well-documented that HRC® may last about 1 year, vegetable oil for several years, and chitin has been shown to facilitate dechlorination for more than 9 months in a low-permeability field application (Figure 2). For variably saturated conditions, solid-phase donors will be especially long-lived.

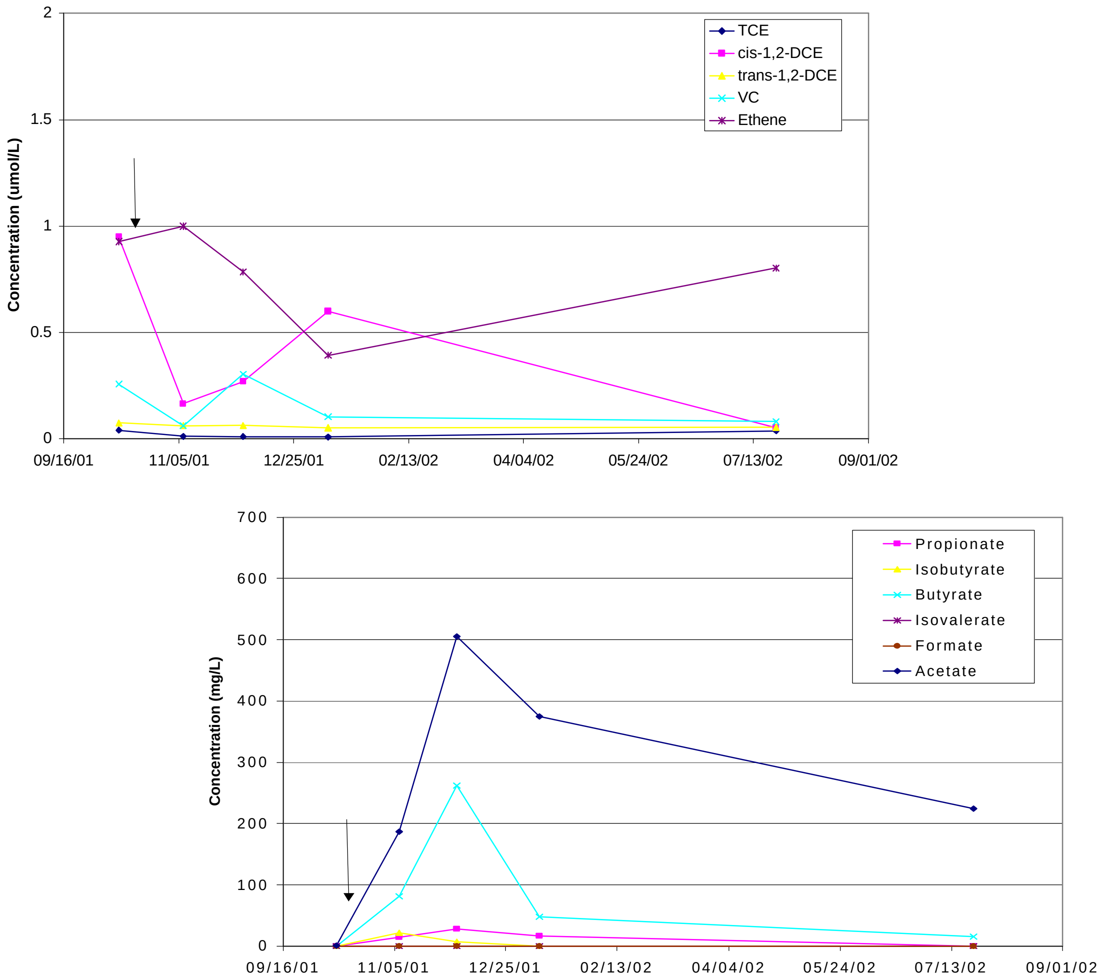

FIGURE 2. Volatile fatty acid production and dechlorination associated with chitin.

The high viscosity and/or nonaqueous nature of most slow-release electron donors limits the ability to distribute them throughout large volumes. Delivery can be achieved through several techniques: a large grid or barrier of closely spaced injection wells, trenching, or soil fracturing. Except for soil fracturing, these techniques are generally cost-effective only in relatively shallow environments. This distribution limitation might be overcome through the use of less viscous emulsions of vegetable oil, LactOil™, or similar substrates.
The effects of slow-release electron donors on bioavailability are highly variable. Nonaqueous liquids such as vegetable oil are likely to sequester contaminants that have an affinity for the organic phase. Solid donors such as chitin and bark mulch will not impact interfacial tension, but should benefit from accelerated dissolution due to biodegradation in the aqueous phase. Donors that combine an immediate decrease in interfacial tension with a longer-term nonaqueous phase may increase bioavailability initially, then sequester remaining contaminants. Work with such donors, including LactOil™, is in the developmental stage.

Conclusions

The general properties of the two classes of electron donors should be matched with site-specific conditions and objectives. Aqueous electron donors are well suited for sites where distribution is challenging (e.g., large, deep, fractured rock, or marginal-permeability sites). Their high solubility and low viscosity allows them to be easily distributed with a minimum number of injection points. Residual source areas where contaminant mass removal is desired are also good applications for aqueous electron donors using B.E.T.™. Another good application is for the purpose of establishing reducing conditions quickly at a site to facilitate complete dechlorination. In this case, an aqueous electron donor could be used in combination with a slow-release electron donor.

Slow-release electron donors are well suited to sites where distribution can be facilitated with a large number of closely spaced wells, especially via direct-push. Emulsified oils or LactOil™ may be more robust because they constitute a “pseudo-aqueous” phase that is somewhat easier to inject. Barriers are another good application for slow-release donors because distribution is required only along a single plane in the aquifer, and it may be undesirable to recharge the barrier with donor frequently. With nonaqueous electron donors, the potential for reduced permeability in the barrier that causes ground water to flow around the barrier should be considered. If long-term contaminant sequestration is acceptable for a residual source area, nonaqueous slow-release donors may be appropriate. Finally, solid slow-release electron donors such as chitin can be very beneficial at variably saturated sites. When the conditions are saturated, volatile fatty acids are released to facilitate dechlorination, but when unsaturated, the electron donor remains in “storage.”

References

Carr, C. S.; Garg, S.; Hughes, J. B. 2000. *Environ. Sci. Technol. 34*, 1088-1094.

Cope, N. and Hughes, J. B. 2001. *Environ. Sci. Technol. 35*, 2014-2021.

Fennell, D. E.; Gossett, J. A.; Zinder, S. H. 1997. *Environ. Sci. Technol. 31*, 918-926.

Sorenson, K. S. 2002. In: *Innovative Strategies for the Remediation of Chlorinated Solvents and DNAPLS in the Subsurface*, S. M. Henry and S. D. Warner eds., ACS Symposium Series 837, ACS Books, Washington, D.C., pp. 119-131.

Yang, Y.; McCarty, P. L. 2000. *Environ. Sci. Technol. 34*, 2979-2984.